(1)

DOE/NASA/51040-41
NASA TM-82920

Evaluation of Dopants in Hydrogen to Reduce Hydrogen Permeation in Candidate Stirling Engine Heater Head Tube Alloys at 760° and 820° C

John A. Misencik
National Aeronautics and Space Administration
Lewis Research Center

October 1982

Prepared for
U.S. DEPARTMENT OF ENERGY
Conservation and Renewable Energy
Office of Vehicle and Engine R&D

NOTICE

DOE/NASA/51040-41
NASA TM-82920

Evaluation of Dopants in Hydrogen to Reduce Hydrogen Permeation in Candidate Stirling Engine Heater Head Tube Alloys at 760° and 820° C

John A. Misencik
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

October 1982

Work performed for
U.S. DEPARTMENT OF ENERGY
Conservation and Renewable Energy
Office of Vehicle and Engine R&D
Washington, D.C. 20545
Under Interagency Agreement DE-AI01-77CS51040

EVALUATION OF DOPANTS IN HYDROGEN TO REDUCE HYDROGEN PERMEATION IN CANDIDATE STIRLING ENGINE HEATER HEAD TUBE ALLOYS AT 760° AND 820° C

John A. Misencik

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

E-1309

SUMMARY

Tubes made of a variety of alloys were pressurized at 21 MPa with hydrogen doped with various amounts of carbon monoxide, carbon dioxide, ethane, ethylene, methane, ammonia, or water. The tubes were then heated in a diesel-fuel-fired Stirling engine materials simulator test rig for 100 hours at 760° and 820° C to determine the effectiveness of the dopants in reducing hydrogen permeation through the hot tube walls. Ultra-high-purity (UHP) hydrogen was used for comparison. The tube alloys were N-155, A-286, Incoloy 800, Nitronic 40, 19-9DL, 316 stainless steel, Inconel 718, and HS-188. The dopant levels were carbon monoxide, 0.2, 0.5, 1, 2, and 5 vol %; carbon dioxide, 0.2, 0.5, 1, 2, and 5 vol %; ethane, 2 vol %; ethylene, 1 vol %; methane, 5 vol %; ammonia, 5 vol %; and water, 40 ppm. Carbon dioxide and carbon monoxide were most effective in reducing hydrogen permeation through the hot tube walls for all alloys. Hydrogen permeation was reduced by as much as two orders of magnitude in some alloys when the gaseous dopants were present, as compared with UHP hydrogen permeation. The remaining dopants (ethane, ethylene, methane, ammonia, and water) were not effective in reducing hydrogen permeation below that achieved with UHP hydrogen. Several alloys were carburized prior to testing with UHP hydrogen. Carburization of the tubes prior to exposure reduced permeation to low values (similar to those for carbon monoxide) of the order of 1.5×10^{-6} $cm^2/sec\ MPa^{1/2}$; however, carbon dioxide was the most effective dopant.

INTRODUCTION

The work described in this report was conducted as a part of the continuing supporting research and technology activities under the DOE-NASA Stirling Engine Highway Vehicle Systems program (ref. 1). Hydrogen, the Stirling engine working fluid, is used at high pressures (21 MPa) and operating temperatures (820° C) to achieve the maximum engine efficiency required for a commercial highway vehicle.

Retention of hydrogen in the heater head tubes at high temperatures is difficult as the hydrogen readily permeates the hot tube walls. Prior work (refs. 2 and 3) has shown that oxygen contents as low as 350 ppm in the hydrogen can substantially reduce hydrogen permeation through the tube walls while in the 760° to 820° C temperature range. Reduction in hydrogen permeation of an order of magnitude has been achieved in some alloys. It has been postulated that this reduction in hydrogen permeation is the result of a thin oxide layer forming on the inner surface of the tube coupled with the formation of a thick adherent oxide layer on the fire side of the tube (refs. 2, 4,

and 5). Another possible cause for the reduced permeation observed in Stirling automotive applications is carburization of the inner surface of the tube by the breakdown of lubricating oils (ref. 5).

In view of the explosive nature of hydrogen-oxygen mixtures, hydrogen with programmed amounts of oxygen cannot be commercially procured. Therefore an alternative method of oxygen supply is required. The work described in this report was conducted to evaluate the effectiveness of doped hydrogen mixtures in preventing the high-temperature (760° or 820° C proposed use-temperature) permeation of hydrogen through tube walls of the currently used N-155 alloy and several candidate heater tube alloys (A-286, Incoloy 800, Nitronic 40, 19-9DL, 316 stainless steel, and Inconel 718). In addition, the cobalt-base alloy HS-188 was investigated to provide a comparison with a nickel-base alloy (Inconel 718) and the six iron-base alloys. Formation of an oxidized, carburized, or nitrided surface layer on the tube inner surface was postulated to be an effective means of reducing hydrogen permeation through the tube walls.

EXPERIMENTAL PROCEDURES

Materials

The eight alloys used in this study were obtained commercially in the form of tubing with an outside diameter of 4.8 mm and an inside diameter of 3.2 mm. Tubes from five of the eight alloys were fabricated by weld drawing: N-155, 19-9DL, Nitronic 40, Inconel 718, and HS-188. Tubes from three alloys were seamless: A-286, Incoloy 800, and 316 stainless steel.

Chemical analyses of the alloys as reported by the fabricators are shown in table I. Five alloys (N-155, A-286, Incoloy 800, Nitronic 40, and 19-9DL) were iron-base alloys with substantial amounts of nickel and chromium. One alloy (316) was a stainless steel. One alloy (Inconel 718) was a nickel-base alloy, and one (HS-188) was a cobalt-base alloy. Average grain size ranged from 7 μm for HS-188 to 73 μm for A-286.

Chemical analyses of the hydrogen and of the hydrogen doped with various gases are shown in table II. These include ultra-high-purity (UHP) hydrogen; hydrogen doped with 0.2, 0.5, 1, 2, and 5 vol % carbon monoxide; hydrogen with similar amounts of carbon dioxide; hydrogen with 2 vol % ethane; hydrogen with 1 vol % ethylene; hydrogen with 5 vol % methane; hydrogen with 5 vol % ammonia; and hydrogen with 40 ppm water.

Stirling Engine Simulator Rig

The Stirling engine simulator rig used in this study was the same as that used in the endurance runs described in references 2 and 3. The rig consists primarily of a combustion gas heating chamber with auxiliary heating control and gas management systems. A schematic drawing of the heating chamber is shown in figure 1. A detailed description of the rig and its operation is given in reference 2.

A dopant run consisted of a series of 5-hour cycles to obtain a total time at temperature of 100 hours. The dopant runs were conducted at 760° and 820° C.

A typical heating cycle consisted of a 6- to 10-minute preheat to the operating temperature, a 5-hour hold at temperature, and then a cooldown to near room temperature. The cooldown time between cycles was 1 hour or longer. After cooldown to about 25° C, the tubes were vented, the transducer was rezeroed, and the tubes were refilled. The pressure readings used for permeation calculations were made at the start of each 5-hour cycle (approx 10 to 15 min into the cycle) and at the end of 5 hours at temperature, just prior to cooldown.

RESULTS AND DISCUSSION

Pressure-Time Relationships

Hydrogen pressure-time data for the N-155 alloy during five selected cycles of the 100-hour runs with UHP hydrogen and with hydrogen doped with 1 vol % carbon dioxide are shown in table III. The 5-hour cycles selected were for 0-5, 20-25, 45-50, 70-75, and 95-100 hours. The data are shown in figure 2. The figure shows a rapid rise in pressure, to 18 tO 21 MPa usually within 10 minutes, and then a decay in pressure during the remainder of the 5-hour cycle. This pressure decay with time at temperature results from hydrogen permeating through the hot tube walls. The rate of pressure decay varied with alloy, dopant species, species concentration, and time during the exposure run. Figure 2(a) shows that for N-155 with UHP hydrogen, the pressure was substantially below 1 MPa after 4 hours and nearly zero after 5 hours for each of the cycles shown, an indication of rapid hydrogen loss through the hot tube wall. Figure 2(b), also for N-155 but with hydrogen doped with 1 vol % carbon dioxide, shows that the pressure drop for the first 5-hour cycle (0-5) was similar to that with UHP hydrogen. However, the pressure drops for the 20-25, 45-50, 70-75, and 95-100 hour cycles were greatly reduced, dropping to 4.3 MPa after the 20-25 hour cycle, to 10.3 MPa after the 45-50 hour cycle, to 13.8 MPa after the 70-75 hour cycle, and to only 15 MPa after the 95-100 hour cycle. Thus, it can be seen that the addition of 1 vol % carbon dioxide to the hydrogen was effective in reducing hydrogen permeation through the hot tube walls.

Hydrogen Permeation

The permeation coefficient φ was calculated for each 5-hour cycle for each alloy throughout the 100-hour dopant run by using the data from the pressure drop curves and the equation from reference 2:

$$P = P_o^{1/2} - \varphi \frac{AP_s Tt}{2\ell V T_s}$$

where

P	pressure in closed system, MPa
P_o	original pressure, MPa
A	permeated area, cm^3
P_s	standard pressure, MPa
T	temperature of system, K
t	time, sec
ℓ	membrane thickness, cm

"Page missing from available version"

Hydrogen doped with carbon dioxide ($H_2 + CO_2$). - The calculated permeation coefficients for the alloys pressurized at 760° and 820° C with hydrogen doped with various percentages of carbon dioxide are shown in tables IV (a), (e), (g), and (h). The carbon dioxide levels in hydrogen were 0.2, 0.5, 1, 2, and 5 vol %. The tube alloys were N-155, A-286, Incoloy 800, Nitronic 40, 19-9DL, Inconel 718, and HS-188.

During the dopant runs there was a substantial reduction in hydrogen permeation for all of the alloys after 100 hours. The data for each alloy are shown in figure 5.

To clarify the large amount of data the permeation coefficients for five alloys (N-155, A-286, Incoloy 800, 19-9DL, Inconel 718, and HS-188) after 5, 25, 50, 75, and 100 hours were averaged for various dopant levels. These results are shown in figure 6. All levels of carbon dioxide were effective in reducing permeation during runs from 5 hours to 100 hours, with the dopant level of 0.2 vol % being least effective and the 1 and 2 vol % being most effective.

Permeation coefficients obtained at 820° C with carbon monoxide and carbon dioxide at various dopant levels are compared in figure 7. This comparison is for the same five alloys compared in figure 6. Dopant levels of carbon monoxide and carbon dioxide above 2 vol % had the same mean permeation. However, less than 2 vol % carbon dioxide resulted in a lower mean permeation.

Hydrogen doped with ethane ($H_2 + C_2H_6$), ethylene ($H_2 + C_2H_4$), or methane ($H_2 + CH_4$). - The calculated permeation coefficients for hydrogen with dopants having the potential to form a carburized layer (ethane, ethylene, and methane) are summarized in tables IV(a) to (c), (e), (g), and (h). The tube alloys used were N-155, A-286, Incoloy 800, 19-9DL, Inconel 718, and HS-188. The dopant runs were conducted at 820° C for 100 hours. The data, plotted in figure 8, show a reduction in permeation with elapsed time. However, the permeation coefficients are not reduced to low levels and are comparable to values obtained with UHP hydrogen (fig. 3). This indicates that the reaction at the inner tube surface with these three dopants in hydrogen did not produce an effective carburized surface barrier to hydrogen permeation through the tube walls.

Hydrogen doped with ammonia ($H_2 + NH_3$). - The calculated permeation coefficients for hydrogen doped with 5 vol % ammonia, a potential nitride former, are shown in tables IV(a) to (c), (e), (g), and (h). The dopant run was begun at 760° C and conducted at this temperature for 50 hours, after which time the temperature was raised to 820° C for an additional 50 hours. The tube alloys used were N-155, A-286, Incoloy 800, 19-9DL, Inconel 718, and HS-188. The calculated φ for these alloys during both segments of the 100-hour run, plotted in figure 9, show a reduction in permeation with elapsed time for both segments of the run. However, the reduction is not to low levels and is comparable to φ obtained with UHP hydrogen (fig. 3) or with hydrogen doped with ethane, ethylene, or methane (fig. 8). This indicates that the reaction of ammonia with the inner surface of the tube did not form an effective nitride surface barrier to hydrogen permeation during the 100-hour run.

Hydrogen doped with water ($H_2 + H_2O$). - The calculated permeation coefficients for the alloys pressurized with hydrogen doped with water (40 ppm) are shown in tables IV(a) to (c) and (e) to (g). The dopant run was conducted at 760° C for 100 hours. The alloys were N-155, A-286, Incoloy 800, 19-9DL, 316 stainless steel, and Inconel 718. The data, plotted in figure 10, show a reduction in permeation with time into the run for all alloys. However, the reductions are not to low levels nor are they as uniform between alloys as those obtained with UHP hydrogen and with hydrogen doped with ethane, ethylene, methane, or ammonia. It appears that the small amount of water in the hydrogen was not effective in forming an oxide on the inner tube surface at 760° C.

Carburized tubes. - The calculated permeation coefficients for the alloys that were pack carburized prior to exposure to UHP hydrogen are shown in tables IV(a) to (c), (e), (g), and (h). The run was conducted at 760° C for 100 hours. Prior to the run the tubes were pack carburized in charcoal treated with an energizer (carbonates of barium, sodium, and calcium). The carburization was accomplished in 7-1/2 hours at 982° C.

The calculated permeation coefficients, plotted in figure 11, show that carburization prior to hydrogen exposure was effective in reducing the permeation to low levels even at the start of the run (first 5 hr). There was, however, little further reduction in hydrogen permeation during the latter part of the run in all alloys except 19-9DL, where a very low permeation coefficient (0.5×10^{-6} $cm^2/sec\ MPa^{1/2}$) was obtained after 100 hours. The low permeation coefficients of the carburized tubes cannot be attributed to the oxide layer that may have formed during the cooldown from the carburization process. This oxide layer would have tended to be reduced and eliminated during the 100-hour exposure to hydrogen. No general trend to increased permeation was noted for the cycles at the latter part of the run. Thus, it is concluded that carburization is an effective barrier to hydrogen permeation. However, application of a uniform carburization layer on the inner tube surfaces is difficult.

Comparison of all dopants. - In an attempt to make a clearer comparison between all dopants and dopant levels, the mean permeation coefficients for five alloys (N-155, A-286, Incoloy 800, Inconel 718, and HS-188) were calculated and compared. These data are shown in figure 12. It can readily be seen that the mean permeation coefficient φ_m after 100 hours was above 5.0×10^{-6} $cm^2/sec\ MPa^{1/2}$ for pure hydrogen and for hydrogen doped with 40 ppm water, 2 vol % ethane, 1 vol % ethylene, 5 vol % ammonia, and 5 vol % methane. Carburization prior to hydrogen exposure in the rig reduced φ_m to 1.5×10^{-6} $cm^2/sec\ MPa^{1/2}$. The carbon monoxide and carbon dioxide dopants were most effective in reducing φ_m to values below 1.0×10^{-6} $cm^2/sec\ MPa^{1/2}$. It can be seen that at the lower levels of dopant (0.2, 0.5, and 1 vol %), carbon dioxide was the most effective. Based on this, the 1 vol % carbon dioxide dopant was selected for future studies to be conducted in the Lewis simulator rigs.

Tube Failures

There were failures in several alloy tubes during the 100-hour runs with the various dopants. The failure times are listed in table V along with the dopant run in which the failure occurred, the number of failures, and the alloy that failed. All of the failures were in three alloys: Incoloy 800, Nitronic 40, and A-286. The time to failure varied from 36-1/2 hours for A-286

in the H_2 + 1 vol % CO_2 run to 99 hours for Nitronic 40 in the H_2 + 0.5 vol % CO run. The tube failures occurred generally in the dopant runs with carbon monoxide and carbon dioxide; however, there was one tube failure (Incoloy 800) in the run with ultra-high-purity hydrogen and one (also Incoloy 800) in the dopant run with H_2 + ethane. As the pressures were usually maintained higher in the carbon monoxide and carbon dioxide dopant runs, the large number of failures in these runs is not surprising, and the failures in Nitronic 40 and Incoloy 800 at short exposure times were not unexpected as failures occurred early in the two previous endurance runs at 760° and 820° C (refs. 2 and 3). The early failures in A-286 during the dopant runs with carbon monoxide and carbon dioxide were not expected as this alloy had a lifetime of 150 to 170 hours during the endurance run at 820° C and 21 MPa when pressurized with helium. Examination of the microstructures of the cross sections of the A-286 tubes indicated that a reaction between the tube surface and the carbon monoxide or carbon dioxide dopant had occurred (fig. 13). Figure 13(a) shows the tube cross section at a magnification of 100. Note that the outside edge had an adherent oxide scale. The inner surface of the tube had been affected to 20 percent of the wall thickness. Figure 13(b) shows the affected area at a magnification of 500. There were two distinct "layers" in the affected area. Another surface effect was found in A-286 during the dopant run with 2 vol % carbon monoxide. In this case, the inner surface of the tube actually peeled away (fig. 14). The cause for this behavior with A-286 when pressurized with hydrogen doped with carbon monoxide has not been determined. This surface reaction may be the cause of the early failures of A-286 in the carbon monoxide and carbon dioxide dopant runs.

Microstructure

Metallographic specimens were sectioned from a hairpin from each module after exposure. The specimens, sectioned from the hottest zone of the tube (approx 17 cm from the bend), were polished, etched, and then examined at magnifications of 100 and 500. Metallographic examination of the outer surface of the tubes revealed an oxide layer on the tubes made of most alloys. This result of reaction with the fire-side environment contributed to the reduction of hydrogen permeation in all alloys. With ultra-high-purity hydrogen all alloys showed a reduction of hydrogen permeation (fig. 3), and this can only be the result of the fire-side oxide as no inner surface reaction was expected nor was any found. Figure 15, which shows the inner surface of N-155 at a magnification of 500, shows no oxide or any surface reaction with UHP hydrogen.

Metallographic examination revealed that several of the dopants did react extensively with the inner surface of several alloy tubes. The extent of this reaction can be seen in figure 16. This figure shows the cross sections of the N-155 alloy after exposure to hydrogen containing 2 vol % ethane and hydrogen containing 1 vol % ethylene, respectively. These cross sections at a magnification of 100 show that the reaction extended to one-third of the wall thickness. The inner surfaces, shown in figure 17 at a magnification of 500, appear to be carburized and have extensive grain boundary carbides. The dopants methane (5 vol %) and ammonia (5 vol %) also exhibited the extensive reaction with most alloys. However, the extensive grain boundary carbides were not found with methane. The surface reaction with methane and ammonia dopants and the apparent carburization with ethane and ethylene dopants were not effective in reducing hydrogen permeation in any of the alloys.

The carbon dioxide and carbon monoxide dopants were most effective in reducing hydrogen permeation through the hot tube walls. Metallographic examination of the tubes after exposure with these dopants revealed varying amounts of oxide on the inner surface of the tubes. One of the most effective dopants was 1 vol % carbon dioxide. A photomicrograph of the inner surface of N-155 at a magnification of 500 is shown in figure 18. Note that there is a very fine oxide layer at the surface, with little or no base metal reaction. With large amounts of carbon dioxide dopant (5 vol %), some base metal reaction was noted (fig. 19). This was also found with the 5 vol % carbon monoxide dopant.

CONCLUSIONS

From the results of an experimental investigation to determine the effects of various dopants in hydrogen to reduce hydrogen permeation through candidate Stirling engine heater tube walls, the following conclusions were drawn:

1. Both carbon monoxide and carbon dioxide were effective in reducing hydrogen permeation through all of the alloys studied.

2. Carbon dioxide was most effective in reducing hydrogen permeation when the dopant levels were at the 0.2 vol % level.

3. Carburization prior to rig exposure reduced hydrogen permeation to the low levels achieved with carbon monoxide; however, carbon dioxide was the most effective dopant.

4. Ultra-high-purity hydrogen and hydrogen doped with water, ethane, ethylene, methane, or ammonia exhibited similar permeation coefficients, indicating that these dopants were not effective in reducing hydrogen permeation to the required low level of approximately 1.0×10^{-6} cm^2/sec $MPa^{1/2}$.

REFERENCES

1. Brogan, J.J.: Highway Vehicle Systems Program Overview. Fifteenth Summary Report, Highway Vehicle Systems Contractors' Coordination Meeting. CONF-771037, 1978, pp. 3-5.

2. Misencik, J.A.: Evaluation of Candidate Stirling Engine Heater Tube Alloys for 1000 Hours at 760° C. DOE/NASA/1040-18, NASA TM-81578, 1980.

3. Misencik, J.A.: Evaluation of Candidate Stirling Engine Heater Tube Alloys at 820° C and 860° C. NASA TM-82837, 1982.

4. Schuon, S.R.; and Misencik, J.A.: Effect of Oxide Films on Hydrogen Permeability of Candidate Stirling Engine Heater Tube Alloys. NASA TM-82824, 1982.

5. Stephens, J.R.: Stirling Materials Developement. Sixteenth Summary Report, Highway Vehicle Systems Contractors' Coordination Meeting. CONF-7904105, 1979, pp. 262-272.

TABLE I. - NOMINAL COMPOSITION OF TUBING ALLOYS

Alloy	Fabrication	Grain size, μm	Cr	Ni	Co	Mn	Mo	W	Ti	Cb+Ta	Si	Al	C	N	Cu	V	Fe
			Composition, wt %														
N-155	Weld drawn	17	21.2	19.9	19.0	1.45	3.0	2.6	---	1.0	0.55	----	0.11	0.16	----	---	(a)
A286	Seamless	73	14.4	24.7	---	1.01	1.2	---	2.1	---	.62	----	.06	----	0.32	0.26	
Incoloy 800	Seamless	66	22.5	32.6	---	.73	---	---	.5	.4	.53	.054	.01	----	.03	---	
Nitronic 40	Weld drawn	15	20.8	7.0	.09	9.36	.03	---	---	---	.49	----	.03	.34	----	---	
316 Stainless steel	Seamless	21	17.3	13.1	---	1.57	2.26	---	---	---	.54	---	.06	---	---	---	
19-9DL	Weld drawn	25	18.3	8.8	---	1.02	1.3	1.2	.3	---	.47	---	.29	---	---	---	
Inconel 718	Weld drawn	26	17.7	53.3	.03	.05	3.02	---	1.12	5.18	.20	.56	.04	---	.04	---	18.5
HS-188[b]	Weld drawn	7	22.0	23.0	Bal	.67	---	13.9	---	---	.38	---	.11	---	---	---	1.79

[a]Balance.
[b]Also contains 0.003 wt % boron and 0.03 wt % lanthanum.

TABLE II. - HYDROGEN DOPANT COMPOSITIONS

Dopant	Component											
	He	N_2	C_2H_6	C_2H_4	O_2	Ar	CO_2	CO	CH_4	H_2O	NH_3	H_2
	Content, vol %											
Carbon monoxide, vol %:												
0.2	---	0.0625	-----	------	0.0036	0	0.0029	0.2027	------	---	----	(a)
0.5	---	.0308	-----	------	.0035	0	.0058	.5506	------	---	----	
1	---	0	-----	------	0	0	0	1.1029	------	---	----	
2	---	------	-----	------	0	------	------	2.0722	0.0118	---	----	
	---	------	-----	------	0	------	------	2.1595	.0123	---	----	
5	---	------	0	0	.0126	.0053	------	5.0097	.00162	---	----	
	---	------	0	0	0	0	------	5.1142	0	---	----	
Carbon dioxide, vol %:												
0.2	0	.0177	-----	------	0	.0233	.1999	------	------	---	----	
0.5	0	.0173	-----	------	.0017	0	.4936	------	------	---	----	
1	---	.0860	-----	------	.0017	.017	1.0028	------	------	---	----	
2	---	.165	-----	------	.0050	.0250	2.1930	------	------	---	----	
5	0	.4424	-----	------	.0044	0	5.073	------	0	---	----	
	---	.0476	-----	------	.0363	0	4.977	------	------	---	----	
	---	.1014	-----	------	.0526	0	4.9348	------	------	---	----	
Ethane (C_2H_6)	0	.8686	1.788	0	------	.0212	0	0	.0451	---	----	
Ethylene (C_2H_4)	0	0	0	.9996	0	0	0	0	0	---	----	
Methane (CH_4)	0	------	-----	------	.0015	0	0	0	5.2320	---	----	
Ammonia (NH_3)	---	------	-----	------	------	------	------	------	------	---	[b]5.0	
Water, ppm	---	------	-----	------	------	------	------	------	------	40	----	
Ultra-high-purity hydrogen	0	0	0	0	0	0	0	0	0	0	0	0

[a]Balance.
[b]Vendor analysis.

TABLE III. - HYDROGEN PRESSURE DECAY FOR N-155 TUBES

FOR FIVE SELECTED CYCLES

(a) Ultra-high-purity hydrogen

Elapsed time in cycle, hr	Cycle time, hr				
	0-5	20-25	45-50	70-75	95-100
	Pressure, MPa				
Start (maximum pressure)	18.8	18.8	18.8	19.7	19.4
1	6.48	10.8	11.2	17.2	10.8
2	1.9	5.6	6.1	6.4	5.4
3	.2	2.6	3.0	2.4	2.4
4	.1	.8	1.1	.9	.8
5	.1	.1	.1	.1	.1

(b) Hydrogen doped with 1 vol % carbon dioxide

Start (maximum pressure)	19.3	20.1	20.1	21.4	20.9
1	6.7	15.0	18.3	19.6	19.5
2	1.7	11.2	15.9	17.8	18.3
3	.2	8.4	14.1	16.4	17.0
4	.1	6.1	12.1	15.0	16.0
5	.1	4.3	10.3	13.8	15.0

TABLE IV. - EFFECT OF DOPANT ON HYDROGEN PERMEATION COEFFICIENT DURING DOPANT RUNS

(a) N-155 alloy tubes

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
		Hydrogen permeation coefficient, φ, 10^6 $cm^2/sec\ MPa^{1/2}$															
Temperature, 820° C																	
5	13.85	13.85	12.95	11.77	10.79	10.8	13.88	14.99	14.44	9.75	7.09	15.5	14.9	---	---	---	---
25	7.62	5.63	2.56	3.70	3.53	3.53	3.29	2.52	4.10	4.58	1.87	6.70	8.09	---	---	---	---
50	6.94	3.47	1.67	1.89	1.75	1.51	1.59	1.86	1.84	2.74	1.24	6.58	7.47	---	8.66	---	---
75	7.19	2.68	1.46	1.54	1.26	1.31	1.21	1.51	1.28	1.85	1.31	5.63	6.82	---	7.22	---	---
100	7.77	2.43	1.22	1.40	1.31	1.18	1.01	1.34	1.01	1.53	1.12	6.07	7.33	---	6.29	---	---
Temperature, 760° C																	
5	---	---	---	---	9.34	10.5	---	---	---	8.56	5.91	---	---	8.56	9.79	12.85	1.48
25	---	---	---	---	7.21	5.14	---	---	---	5.48	3.24	---	---	5.96	6.14	10.03	1.24
50	---	---	---	---	6.23	4.62	---	---	---	5.27	2.34	---	---	5.87	5.63	7.34	1.08
75	---	---	---	---	5.48	3.77	---	---	---	---	2.28	---	---	6.05	---	7.34	.95
100	---	---	---	---	---	3.84	---	---	---	---	2.14	---	---	5.71	---	6.23	.89

(b) A-286 alloy tubes

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
		Hydrogen permeation coefficient, φ, 10^6 $cm^2/sec\ MPa^{1/2}$															
Temperature, 820° C																	
5	19.43	16.84	11.77	14.39	13.88	21.58	15.54	15.54	18.57	12.18	14.40	17.70	18.50	---	---	---	---
25	7.06	7.62	2.25	1.46	1.49	9.48	2.68	1.87	1.17	1.08	4.06	6.37	9.96	---	---	---	---
50	6.37	5.40	1.96	1.38	1.02	7.19	2.25	1.61	---	---	1.63	6.27	9.47	---	9.51	---	---
75	4.92	2.86	1.59	1.55	.93	3.21	2.17	1.23	1.48	.90	1.75	4.03	4.85	---	9.28	---	---
100	5.51	2.69	1.58	1.51	.85	3.11	2.94	1.45	1.27	.73	1.60	4.10	4.82	---	8.3	---	---
Temperature, 760° C																	
5	---	---	---	---	10.03	10.03	---	---	---	12.09	6.32	---	---	11.75	10.82	15.23	3.54
25	---	---	---	---	2.31	3.74	---	---	---	2.45	4.72	---	---	7.61	5.79	---	3.54
50	---	---	---	---	1.60	2.30	---	---	---	1.54	3.95	---	---	6.53	5.41	8.94	3.30
75	---	---	---	---	1.14	1.70	---	---	---	---	3.95	---	---	6.63	---	8.56	2.75
100	---	---	---	---	---	1.23	---	---	---	---	2.74	---	---	6.23	---	9.34	2.52

TABLE IV. - Continued.

(c) *Incoloy 800 alloy tubes*

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
	Hydrogen permeation coefficient, φ, 10^6 cm^2/sec MPa$^{1/2}$																
Temperature, 820° C																	
5	12.95	9.96	2.44	7.93	2.78	2.11	8.27	5.25	1.42	2.52	6.61	16.2	13.4	---	---	---	---
25	8.45	1.29	1.90	1.55	1.39	.61	2.44	3.11	.72	.90	.97	7.93	11.8	---	---	---	---
50	6.82	2.31	1.25	2.06	1.41	.83	2.51	1.09	1.44	.83	.86	---	9.25	---	7.50	---	---
75	4.83	1.69	1.26	1.04	.52	.53	1.49	.60	1.32	.94	.87	3.50	6.53	---	6.29	---	---
100	4.37	1.11	1.05	1.43	.59	.39	.92	.82	.53	.45	---	4.26	5.26	---	5.34	---	---
Temperature, 760° C																	
5	---	---	---	---	4.19	3.37	---	---	---	7.76	2.52	---	---	9.14	9.79	11.42	1.60
25	---	---	---	---	1.11	---	---	---	---	.71	.88	---	---	6.23	5.96	6.23	1.66
50	---	---	---	---	.90	.69	---	---	---	.88	.73	---	---	5.71	5.01	5.96	1.58
75	---	---	---	---	.74	.52	---	---	---	---	.56	---	---	5.71	---	4.95	1.43
100	---	---	---	---	---	.46	---	---	---	---	.60	---	---	5.48	---	4.89	1.42

(d) *Nitronic 40 alloy tubes*

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
	Hydrogen permeation coefficient, φ, 10^6 cm^2/sec MPa$^{1/2}$																
Temperature, 820° C																	
5	---	14.94	13.88	15.54	13.88	11.43	12.14	12.95	13.44	---	---	---	---	---	---	---	---
25	---	.66	.52	.40	1.38	.56	.75	1.20	.48	---	---	---	---	---	---	---	---
50	---	.55	.45	.25	1.60	.56	.77	.64	.44	---	---	---	---	---	---	---	---
75	---	---	.27	.30	.58	.40	.49	.60	.58	---	---	---	---	---	---	---	---
100	---	.35	---	.32	.68	.34	.33	.56	.21	---	---	---	---	---	---	---	---
Temperature, 760° C																	
5	---	---	---	---	---	---	---	---	---	---	7.36	---	---	---	---	---	---
25	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
50	---	---	---	---	---	---	---	---	---	---	.57	---	---	---	---	---	---
75	---	---	---	---	---	---	---	---	---	---	.59	---	---	---	---	---	---
100	---	---	---	---	---	---	---	---	---	---	.51	---	---	---	---	---	---

TABLE IV. - Continued.

(e) 19-9DL alloy tubes

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
		Hydrogen permeation coefficient, φ, 10^6 $cm^2/sec\ MPa^{1/2}$															
Temperature, 820° C																	
5	14.94	---	---	---	---	---	---	---	---	14.44	---	13.9	14.40	---	---	---	---
25	9.48	---	---	---	---	---	---	---	---	4.28	---	8.27	7.19	---	---	---	---
50	8.10	---	---	---	---	---	---	---	---	2.59	---	7.93	6.05	---	5.27	---	---
75	7.77	---	---	---	---	---	---	---	---	2.29	---	6.37	5.40	---	4.48	---	---
100	8.10	---	---	---	---	---	---	---	---	2.33	---	6.27	5.71	---	3.90	---	---
Temperature, 760° C																	
5	---	---	---	---	8.75	8.22	---	---	---	9.56	4.47	---	---	7.61	8.39	9.34	7.36
25	---	---	---	---	6.63	3.67	---	---	---	6.53	2.87	---	---	5.41	3.09	5.08	---
50	---	---	---	---	5.71	2.52	---	---	---	5.71	1.89	---	---	4.89	2.62	4.89	.57
75	---	---	---	---	4.31	1.91	---	---	---	---	1.89	---	---	4.78	---	4.73	.59
100	---	---	---	---	---	1.80	---	---	---	---	1.64	---	---	4.78	---	4.84	.51

(f) 316 Stainless steel alloy tubes

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
		Hydrogen permeation coefficient, φ, 10^6 $cm^2/sec\ MPa^{1/2}$															
Temperature, 820° C																	
5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
25	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
50	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
75	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
100	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Temperature, 760° C																	
5	---	---	---	---	---	13.7	---	---	---	---	---	---	---	---	---	12.85	---
25	---	---	---	---	---	9.34	---	---	---	---	---	---	---	---	---	---	---
50	---	---	---	---	---	7.21	---	---	---	---	---	---	---	---	---	11.75	---
75	---	---	---	---	---	6.53	---	---	---	---	---	---	---	---	---	10.82	---
100	---	---	---	---	---	6.32	---	---	---	---	---	---	---	---	---	10.54	---

TABLE IV. - Concluded.

(g) Inconel 718 alloy tubes

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
	Hydrogen permeation coefficient, φ, 10^6 $cm^2/sec\ MPa^{1/2}$																
Temperature, 820° C																	
5	8.45	16.89	2.11	1.71	0.66	0.79	5.55	1.48	0.72	0.65	1.1	20.4	21.6	---	---	---	---
25	3.81	.22	.24	.46	.31	.32	.26	.21	.27	.28	.83	10.2	11.4	---	---	---	---
50	3.53	.19	.20	.50	.20	.31	.40	.23	.25	.21	.83	8.83	8.63	---	8.86	---	---
75	3.38	.22	.28	.14	.32	.23	.33	.21	.26	.28	.67	7.77	7.77	---	6.96	---	---
100	3.47	.23	.21	.16	.17	.13	.26	.16	.25	.26	.63	7.19	8.63	---	5.82	---	---
Temperature, 760° C																	
5	---	---	---	---	---	0.85	---	---	---	---	1.02	---	---	11.42	6.42	10.82	1.08
25	---	---	---	---	---	---	---	---	---	---	.74	---	---	6.85	5.14	---	.92
50	---	---	---	---	---	.47	---	---	---	---	.67	---	---	6.42	4.78	3.84	.89
75	---	---	---	---	---	.42	---	---	---	---	.60	---	---	6.05	---	2.76	.95
100	---	---	---	---	---	.40	---	---	---	---	.71	---	---	5.48	---	2.05	.99

(h) HS-188 alloy tubes

Time, hr	Ultra-high-purity hydrogen	Dopant															Carburized tubes
		Carbon monoxide, vol %					Carbon dioxide, vol %					Ethane (C_2H_6)	Ethylene (C_2H_4)	Methane (CH_4)	Ammonia (NH_3)	H_2O (40 ppm)	
		0.2	0.5	1.0	2.0	5.0	0.2	0.5	1.0	2.0	5.0						
	Hydrogen permeation coefficient, φ, 10^6 $cm^2/sec\ MPa^{1/2}$																
Temperature, 820° C																	
5	14.39	13.40	13.88	11.77	10.22	10.5	13.40	11.43	11.14	8.12	6.39	13.0	15.5	---	---	---	---
25	8.83	5.98	5.32	3.70	2.12	1.03	6.07	4.22	1.71	1.48	1.24	7.06	9.96	---	---	---	---
50	7.93	4.22	3.60	2.56	1.34	.72	4.13	2.88	1.20	1.03	.83	6.58	9.03	---	8.35	---	---
75	7.62	3.18	2.66	2.15	.93	---	3.08	2.18	.64	.84	.83	5.89	8.45	---	7.09	---	---
100	7.33	2.90	2.23	2.14	.86	.46	2.84	1.76	.78	.69	.61	5.98	8.09	---	6.09	---	---
Temperature, 760° C																	
5	---	---	---	---	7.76	---	---	---	---	---	5.34	---	---	7.91	6.82	---	2.06
25	---	---	---	---	2.19	---	---	---	---	---	1.79	---	---	6.63	5.71	---	1.23
50	---	---	---	---	1.37	---	---	---	---	---	2.80	---	---	6.23	---	---	.94
75	---	---	---	---	.94	---	---	---	---	---	3.00	---	---	6.05	---	---	.82
100	---	---	---	---	---	---	---	---	---	---	1.90	---	---	5.79	---	---	.83

TABLE V. - SUMMARY OF TUBE FAILURES

Dopant run	Number of failed tubes[a]	Alloy	Time to failure, hr
UHP hydrogen	1	Incoloy 800	50
H_2 + 0.2 vol % CO		Nitronic 40	64-1/2
		A-286	80
H_2 + 0.5 vol % CO		Nitronic 40	99
H_2 + 1 vol % CO		Nitronic 40	47
		A-286	48-1/2
H_2 + 2 vol % CO	0		
H_2 + 5 vol % CO	0		
H_2 + 0.2 vol % CO_2	1	Incoloy 800	55
	1	Nitronic 40	57
H_2 + 0.5 vol % CO_2	0		
H_2 + 1 vol % CO_2	2	A-286	36-1/2,47
	2	Nitronic 40	52,60
	2	Incoloy 800	61,65
H_2 + 2 vol % Co_2	1	A-286	44
H_2 + 5 vol % CO_2	1	Incoloy 800	97
H_2 + ethane	1	Incoloy 800	40
H_2 + ethylene	0		
H_2 + methane			
H_2 + ammonia			
H_2 + water			
H_2 + carburized tubes			

[a]Four tubes tested.

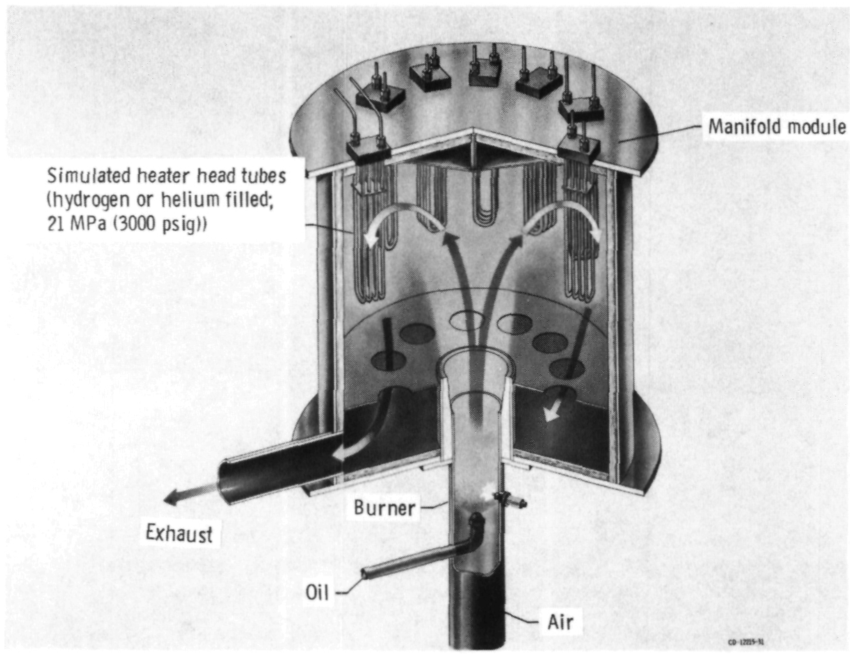
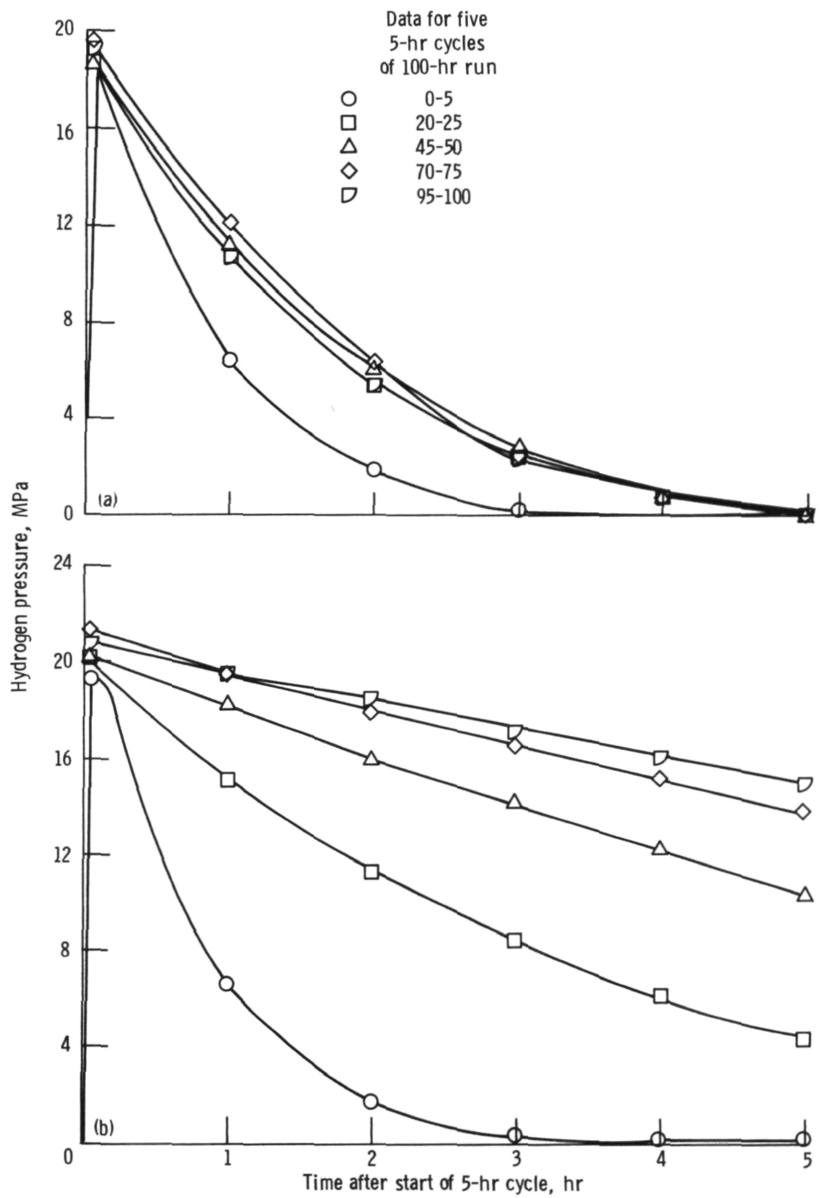


Figure 1. - Schematic representation of Stirling engine simulator materials test rig.



(a) Ultra-high-purity hydrogen.

(b) Hydrogen doped with 1 vol % CO_2.

Figure 2. - Pressure decay curves for N-155 at 820^{0} C.

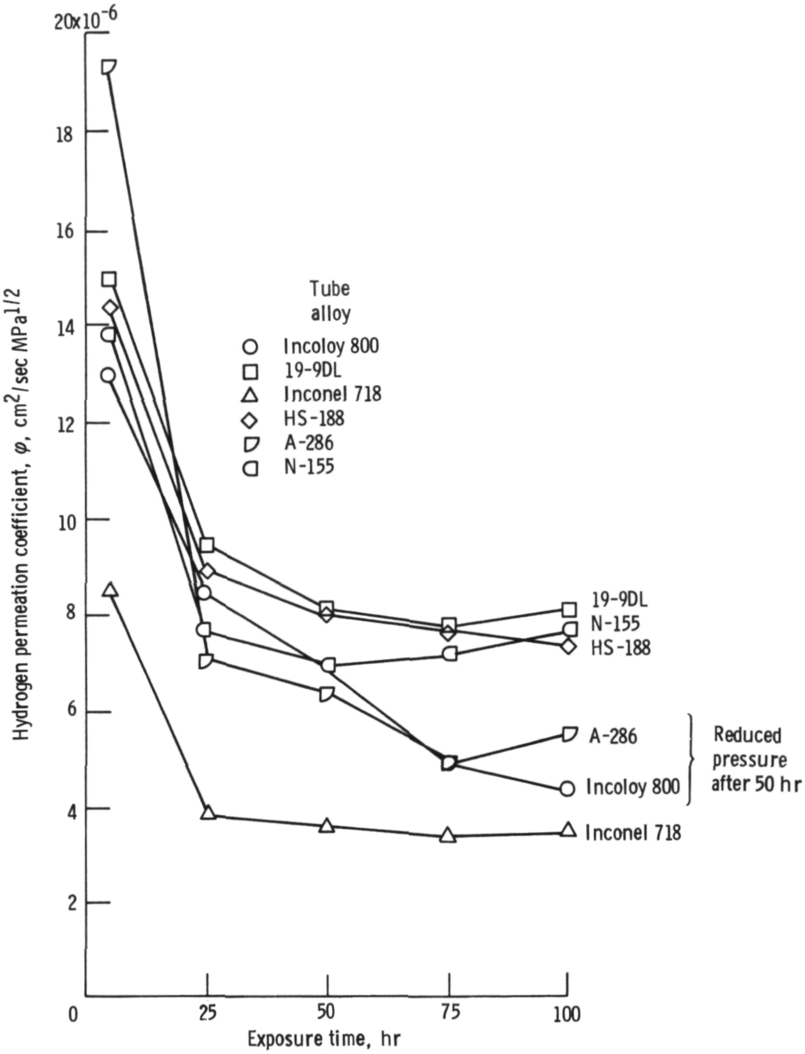
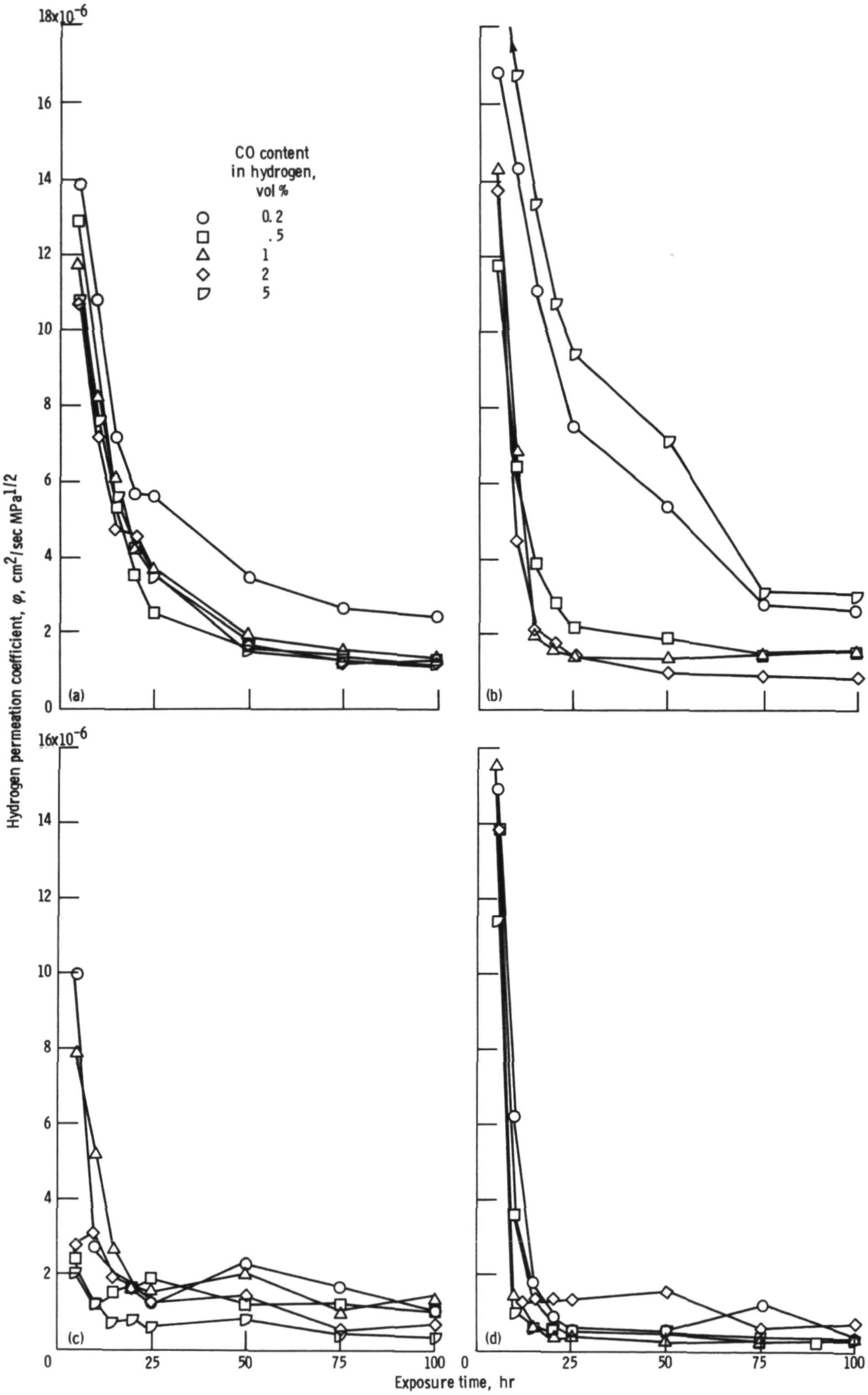
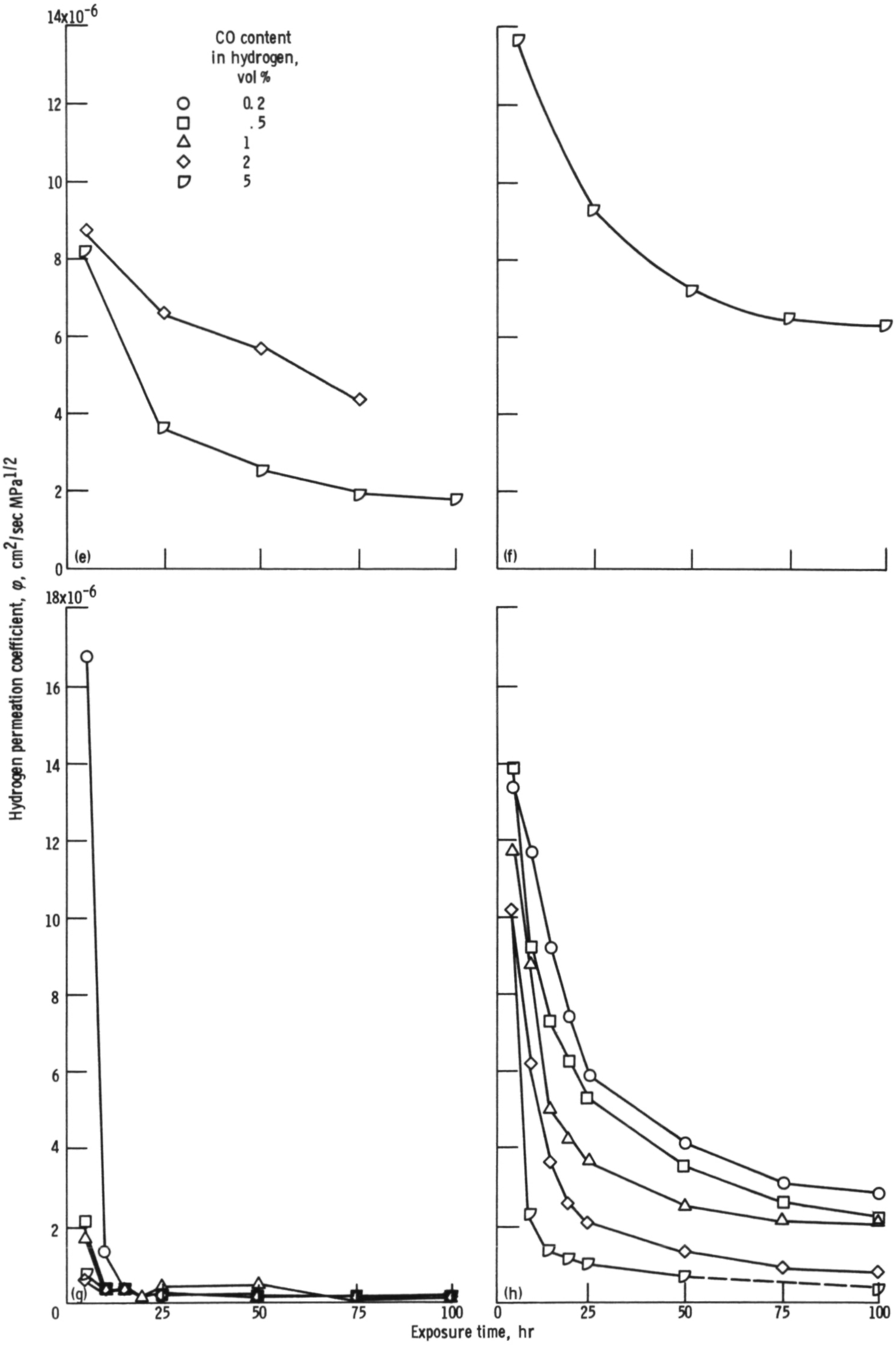


Figure 3. - Permeation coefficient as function of exposure time at 820° C - ultra-high-purity hydrogen in various alloy tubes.



(a) N-155 tubes at 820° C.
(b) A-286 tubes at 820° C.
(c) Incoloy 800 tubes at 820° C.
(d) Nitronic 40 tubes at 820° C.

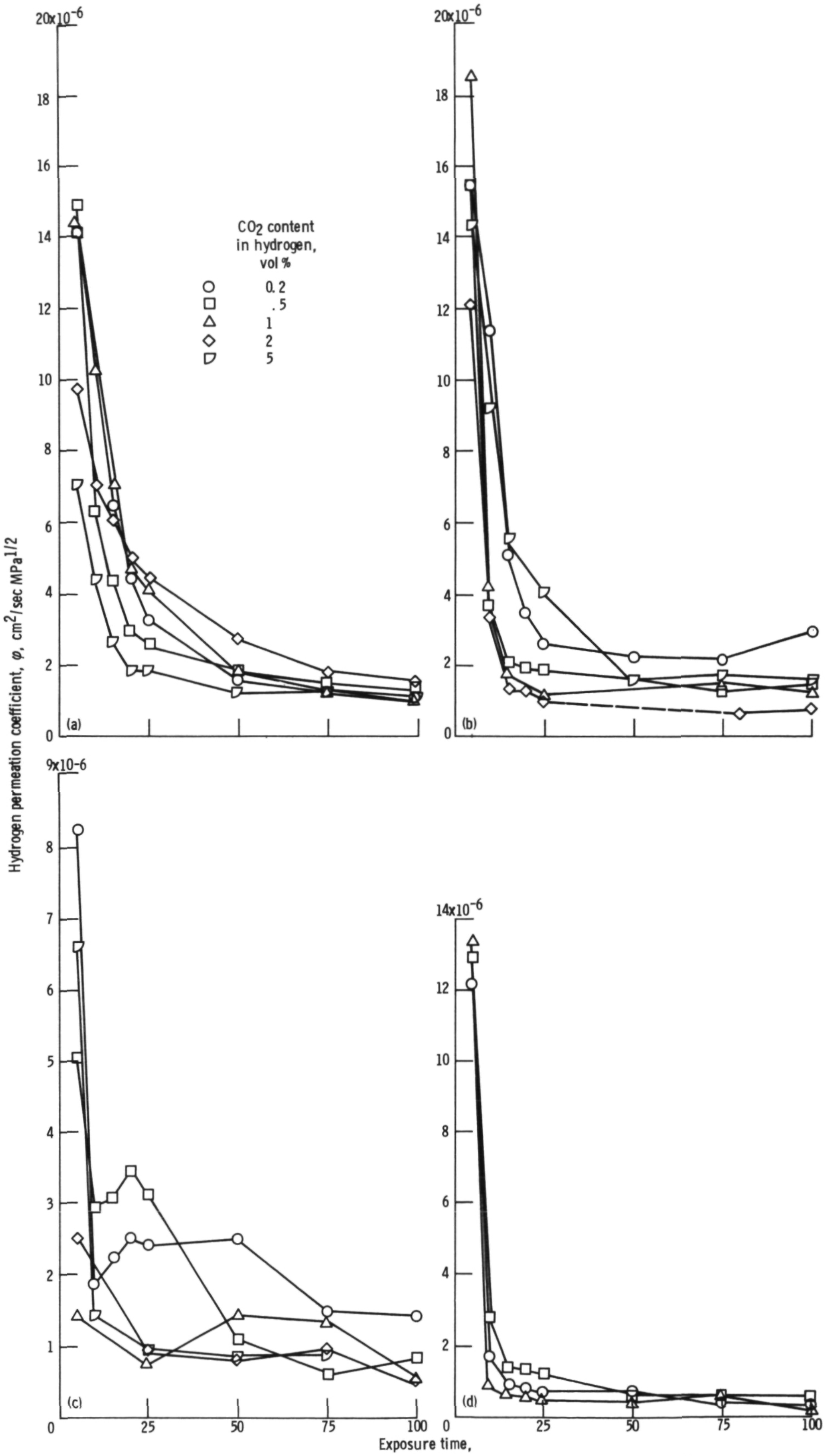
Figure 4. - Permeation coefficient as function of exposure time - carbon monoxide dopant in hydrogen in various alloy tubes.



(e) 19-9DL at 760° C.
(g) Inconel 718 at 820° C.

(f) 316 Stainless steel at 760° C.
(h) HS-188 at 820° C.

Figure 4. - Concluded.



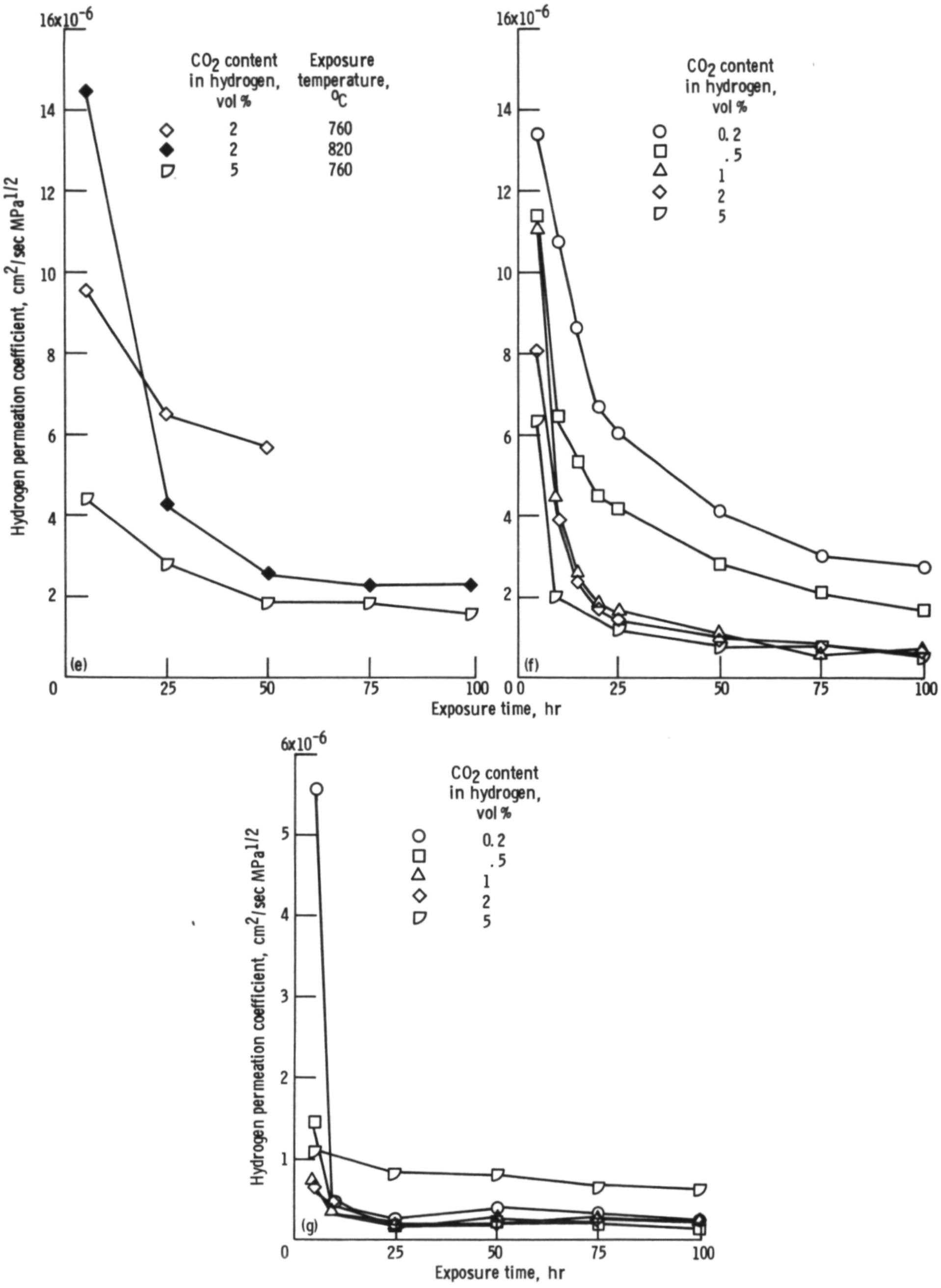
(a) N-155 alloy at 820° C.

(b) A-286 alloy at 820° C.

(c) Incoloy 800 at 820° C.

(d) Nitronic 40 at 820° C.

Figure 5. - Permeation coefficient as function of exposure time - carbon dioxide dopant in hydrogen in various alloy tubes.



(e) 19-9DL at 760° C and 820° C. (f) HS-188 at 820° C.

(g) Inconel 718 at 820° C.

Figure 5. - Concluded.

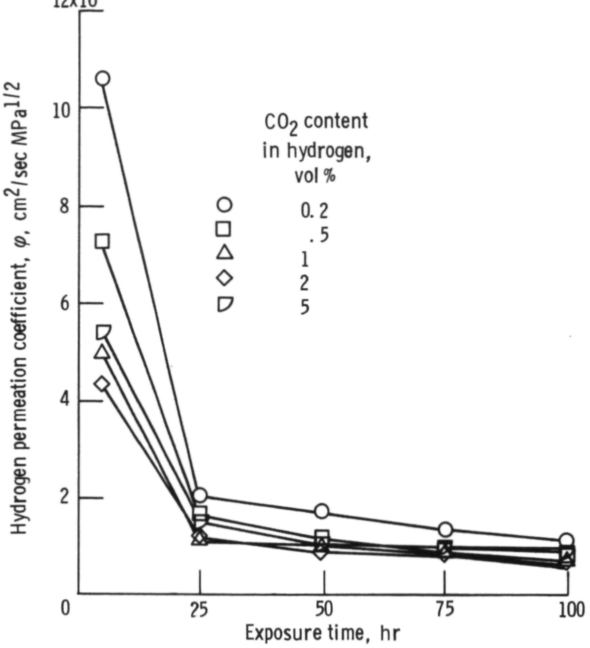


Figure 6. - Average permeation coefficient as function of exposure time at 820° C - carbon dioxide dopant in hydrogen; average for Incoloy 800, A-286, HS-188, Inconel 718, and N-155 tubes.

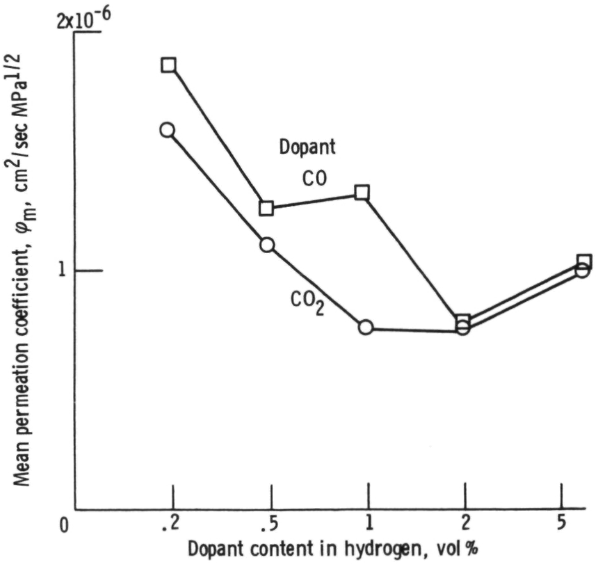
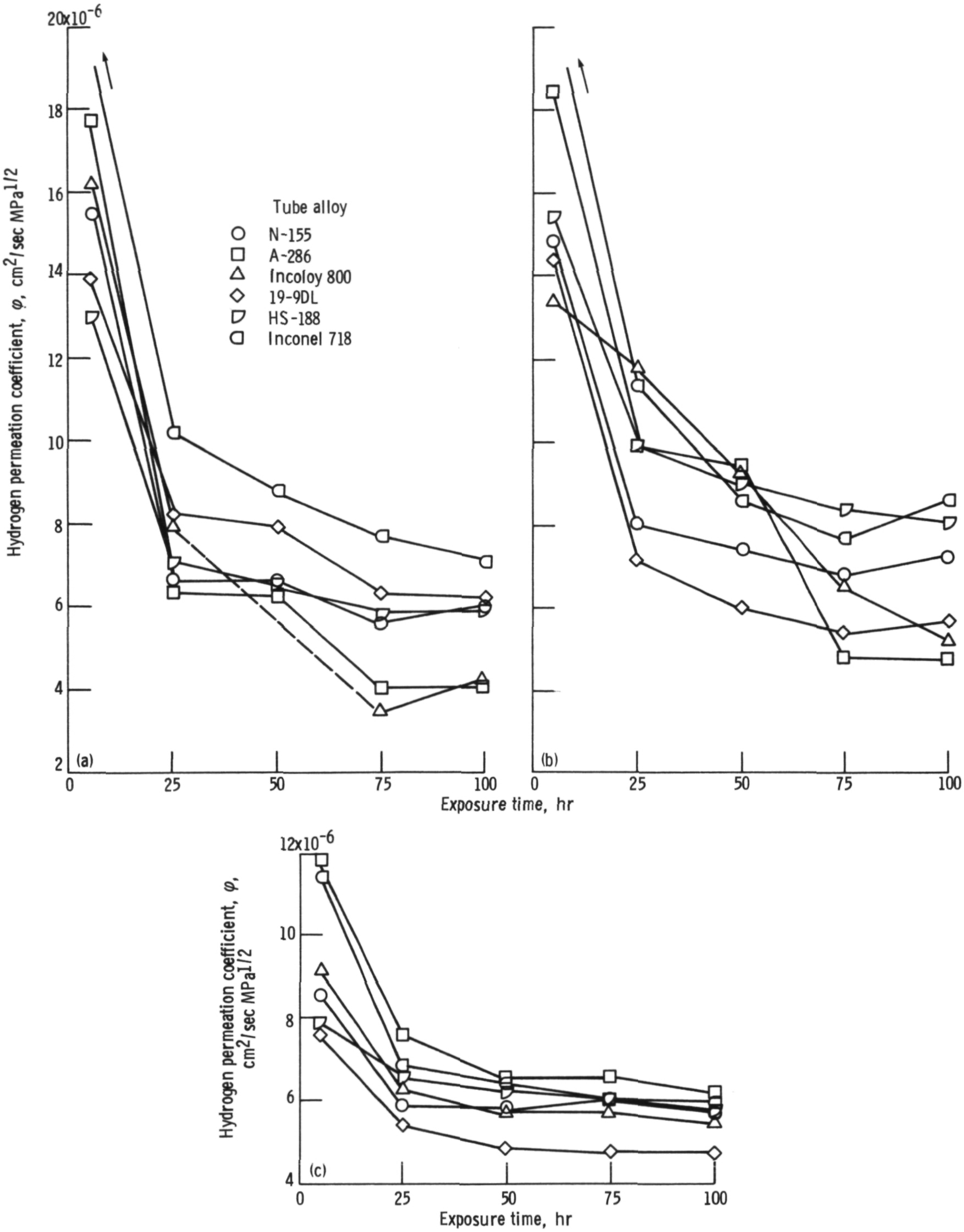


Figure 7. - Mean permeation coefficient after 100 hours as function of dopant content in hydrogen. Dopants, CO and CO_2.



(a) 2 vol % ethane in hydrogen. (b) 1 vol % ethylene in hydrogen.

(c) 5 vol % methane in hydrogen.

Figure 8. - Permeation coefficient as function of exposure time at 820° C - ethane, ethylene, and methane dopants in hydrogen in various alloy tubes.

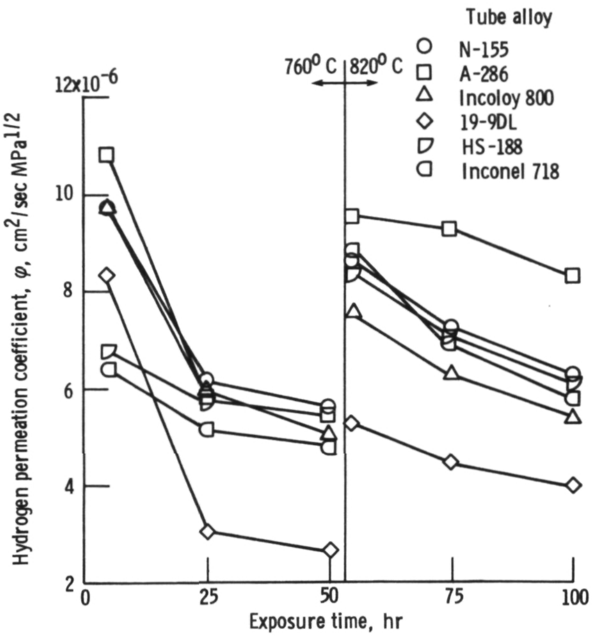


Figure 9. - Permeation coefficient as function of exposure time at 760⁰ and 820⁰ C - ammonia dopant in hydrogen in various alloy tubes.

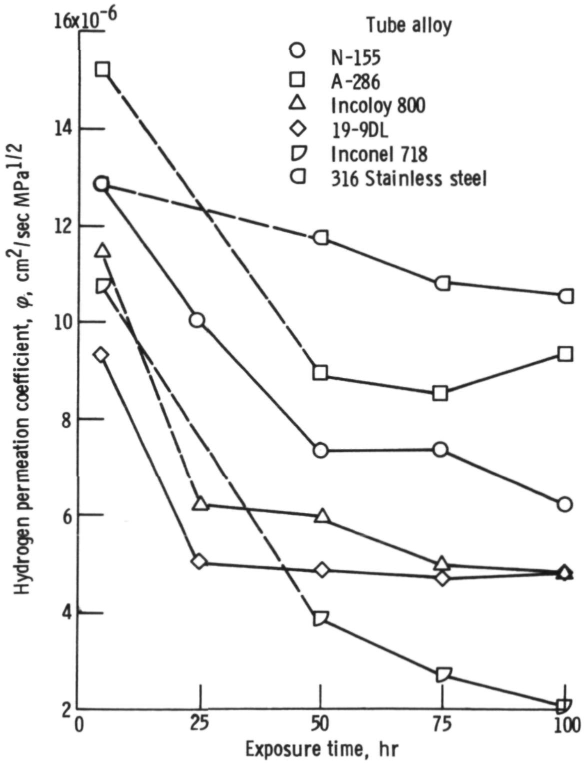


Figure 10. - Permeation coefficient as function of exposure time at 760⁰ C - water dopant in hydrogen in various alloy tubes.

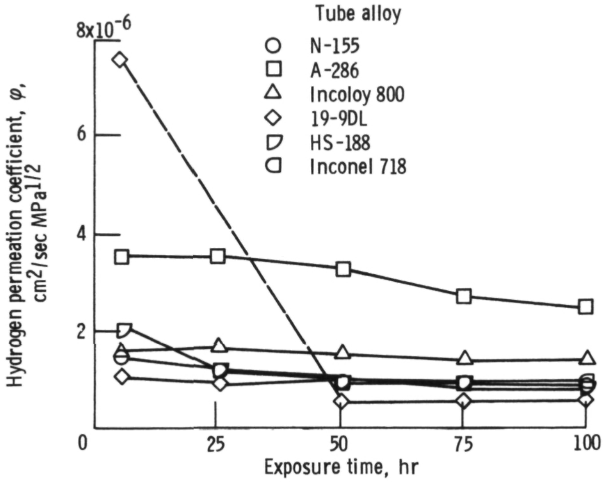


Figure 11. - Permeation coefficient as function of exposure time at 760° C - ultra-high-purity hydrogen in carburized tubes.

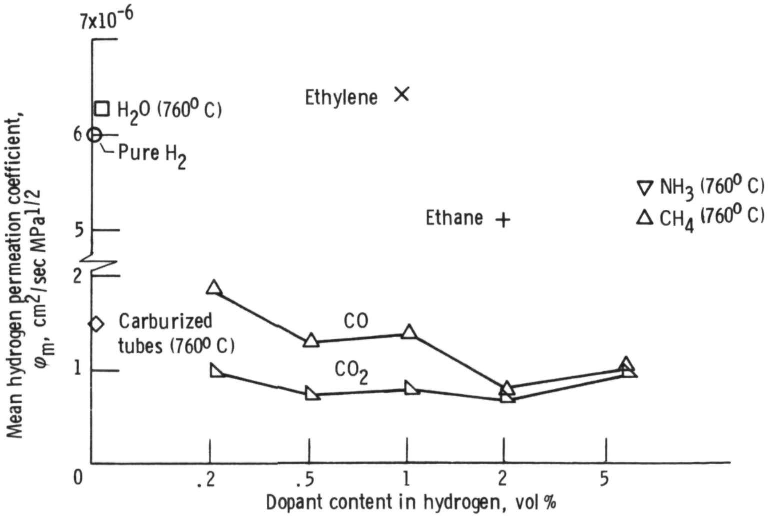
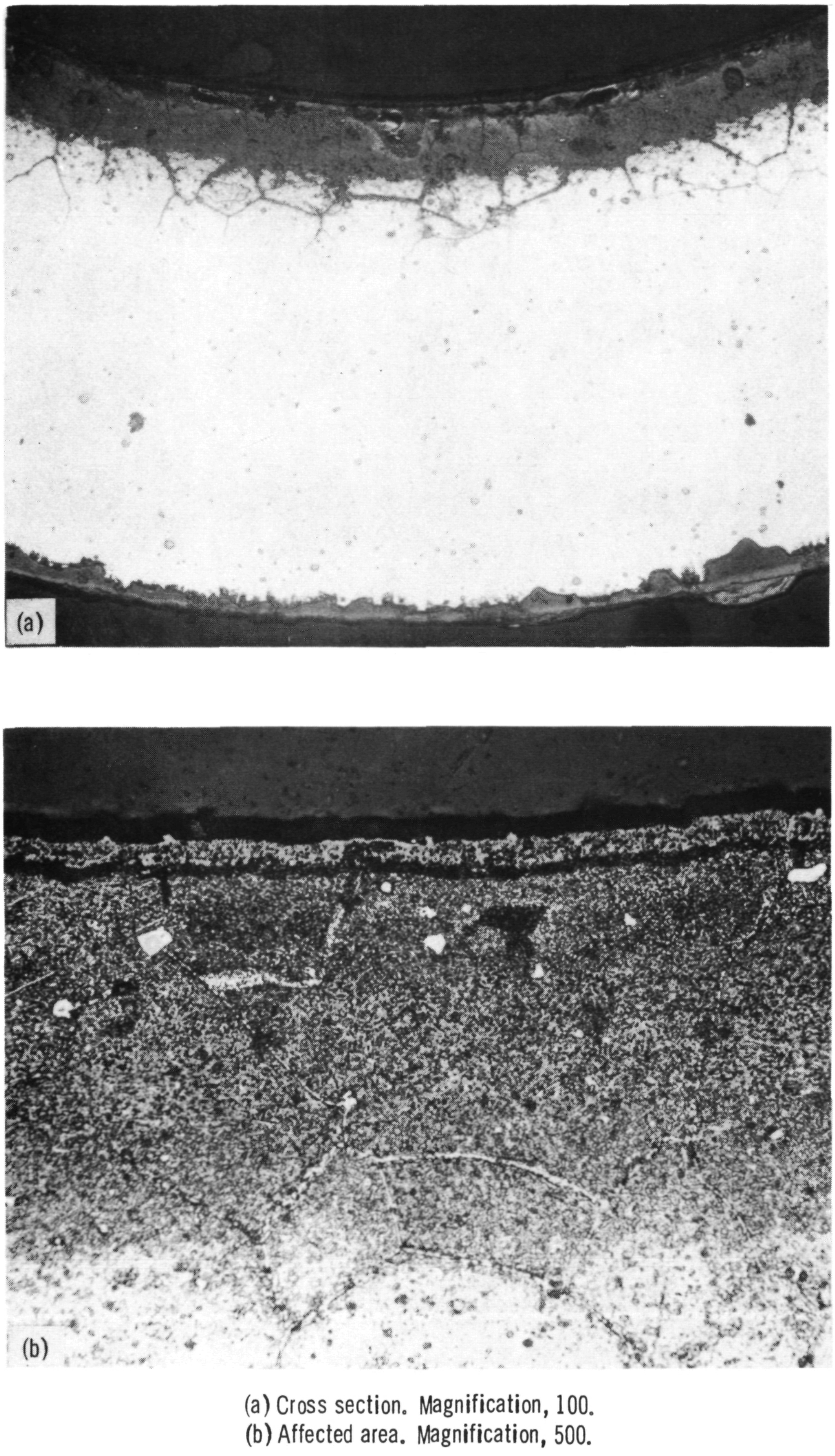


Figure 12. - Mean permeation coefficient as function of dopant content in hydrogen after 100-hr exposure. Exposure temperature, 820° C except where noted. (See text for alloys used in a specific dopant run.)



(a) Cross section. Magnification, 100.
(b) Affected area. Magnification, 500.

Figure 13. - Microstructure of A-286 tube cross section after 100-hr exposure to hydrogen doped with 5 vol % carbon monoxide at 820° C.

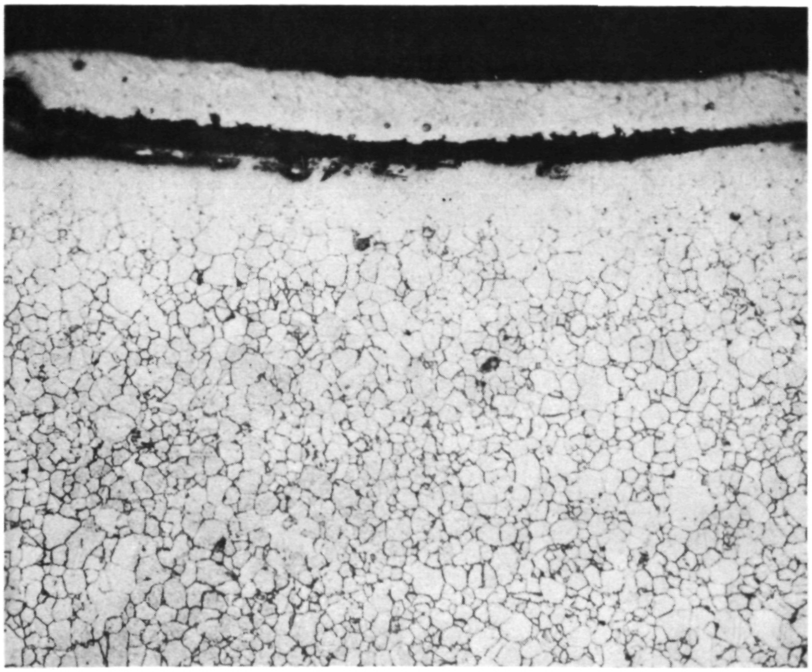


Figure 14. - Microstructure of A-286 tube inner surface after 100-hr exposure to hydrogen doped with 2 vol % carbon monoxide at 820° C. Magnification, 500.

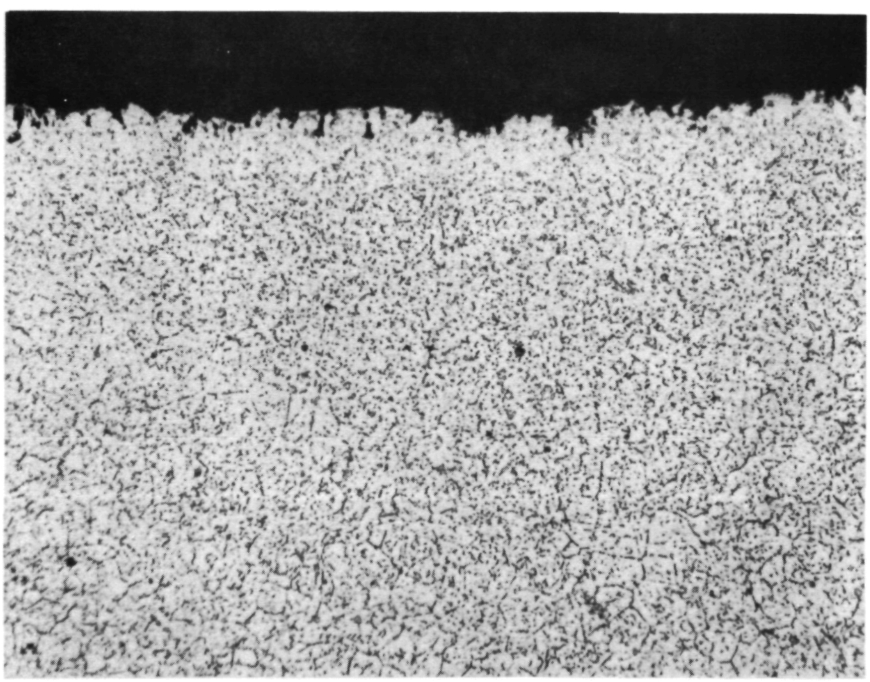
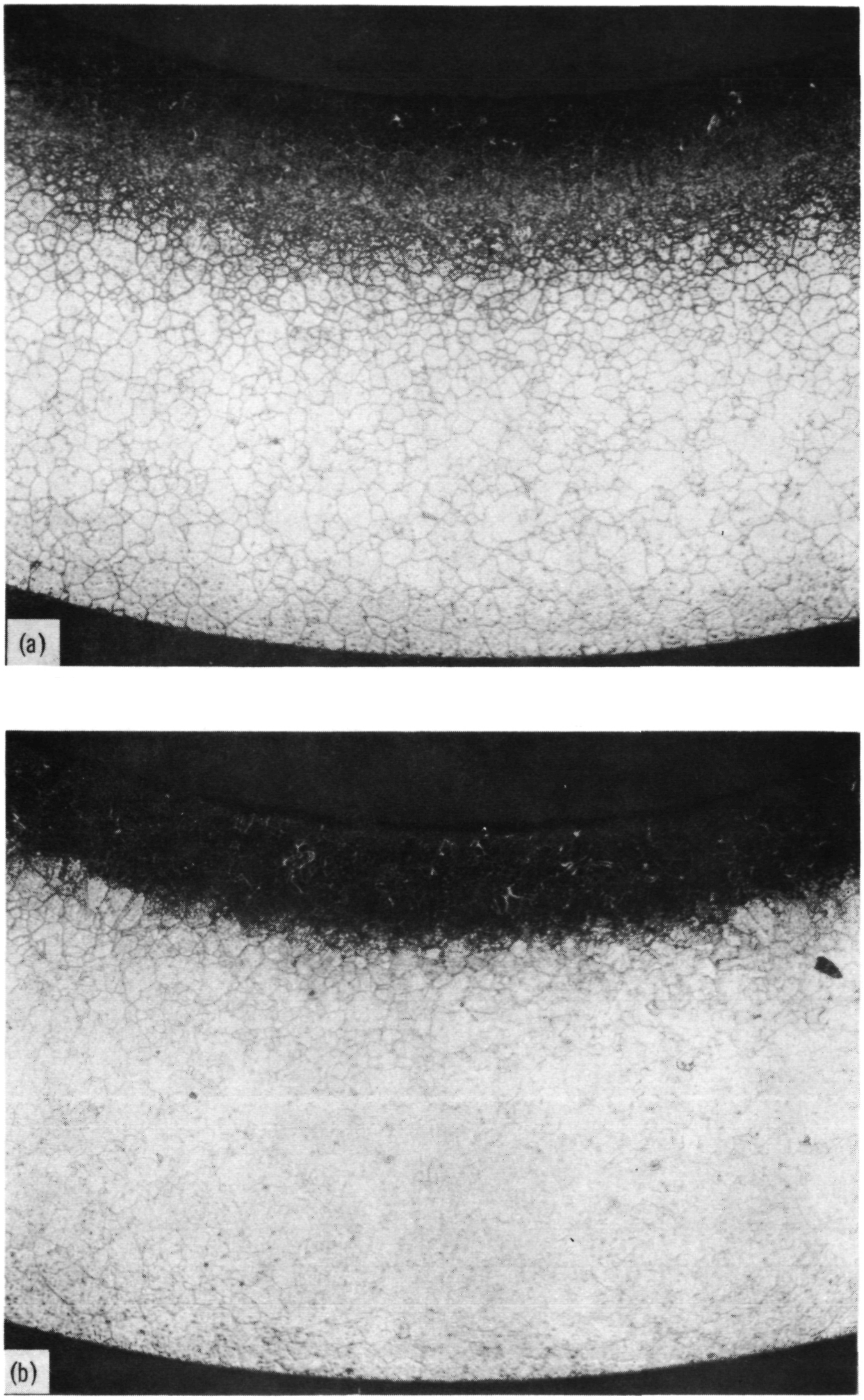
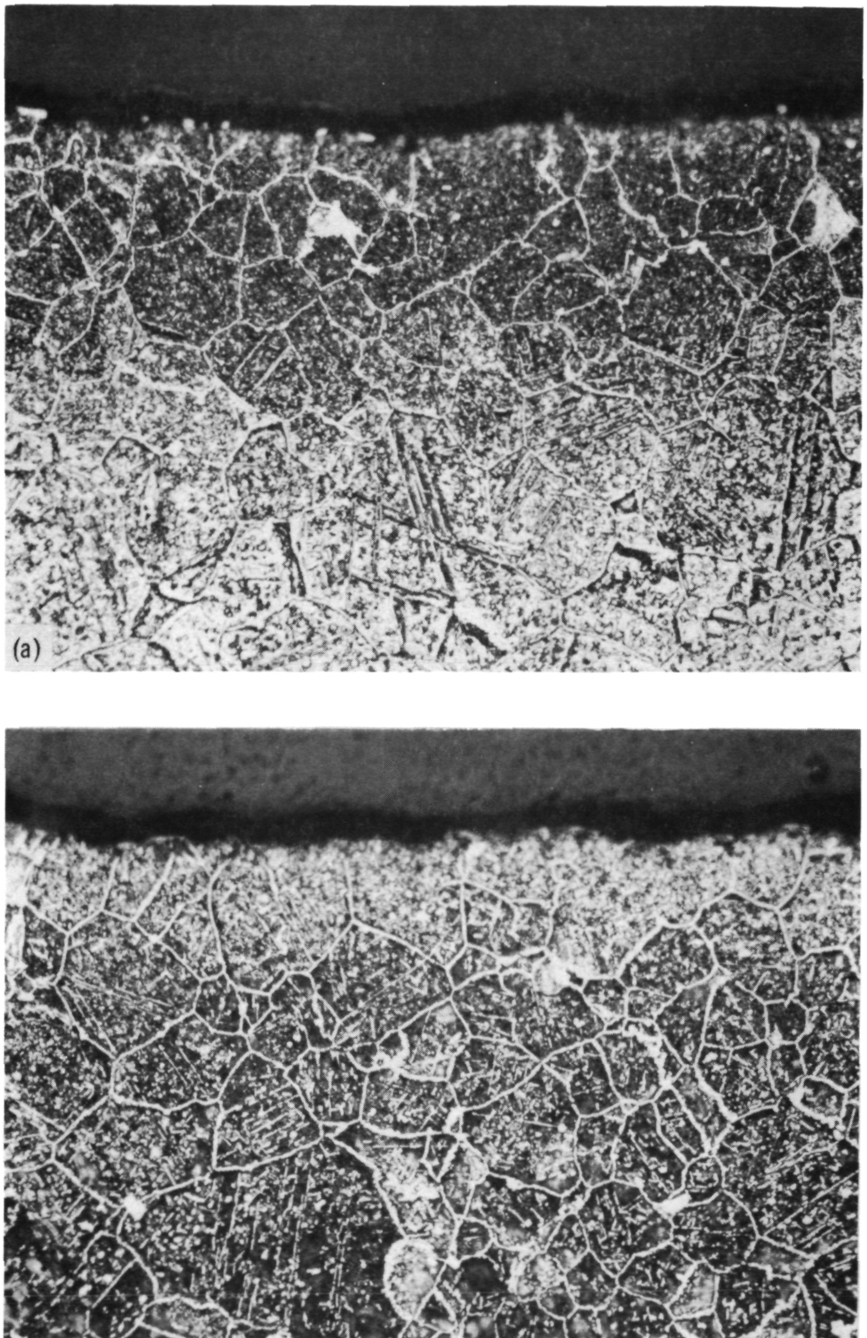


Figure 15. - Microstructure of N-155 tube inner surface after 100-hr exposure to ultra-high-purity hydrogen at 820° C. Magnification, 500.



(a) 2 vol % ethane in hydrogen
(b) 1 vol % ethylene in hydrogen.

Figure 16. - Microstructure of N-155 tube cross sections after 100-hr exposure to hydrogen doped with ethane or ethylene at 820° C. Magnification, 100.



(a) 2 vol % ethane in hydrogen.
(b) 1 vol % ethylene in hydrogen.

Figure 17. - Microstructure of N-155 tube inner surfaces after 100-hr exposure to hydrogen doped with ethane or ethylene at 820° C. Magnification, 500.

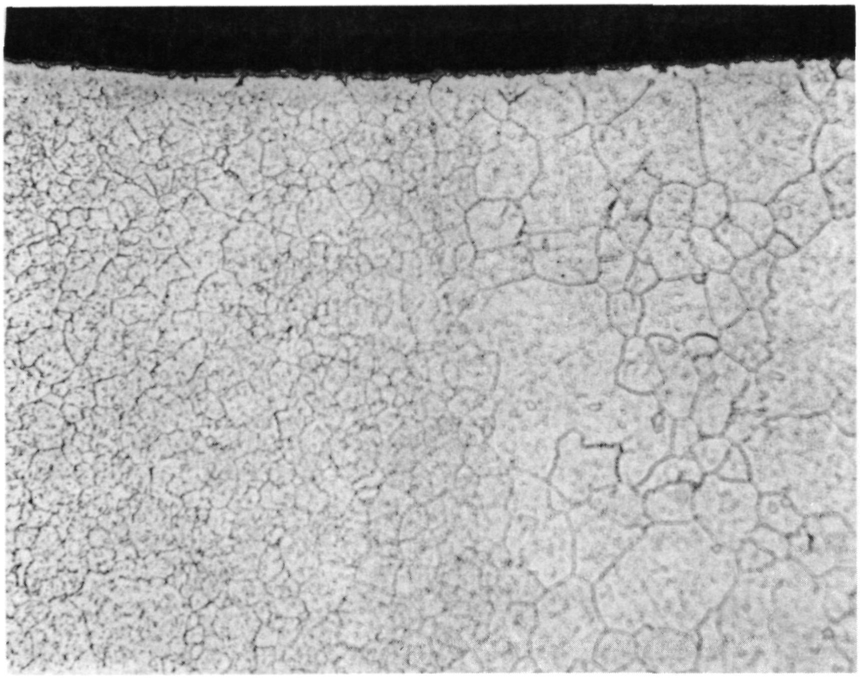


Figure 18. - Microstructure of N-155 tube inner surface after 100-hr exposure to hydrogen doped with 1 vol % carbon dioxide at 820° C. Magnification, 500.

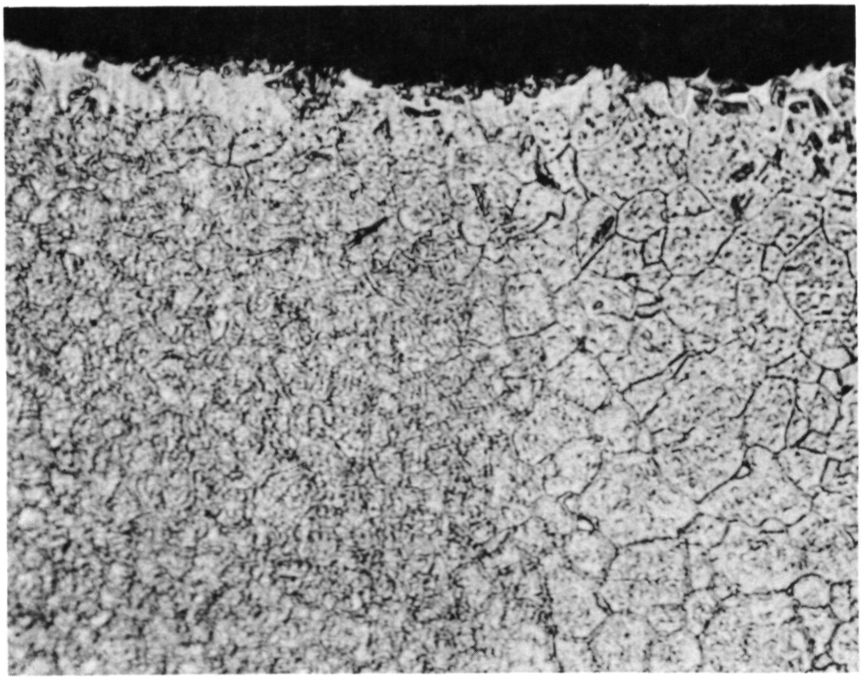


Figure 19. - Microstructure of N-155 tube inner surface after 100-hr exposure to hydrogen doped with 5 vol % carbon dioxide at 820° C. Magnification, 500.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-82920		

4. Title and Subtitle	5. Report Date
EVALUATION OF DOPANTS IN HYDROGEN TO REDUCE HYDROGEN PERMEATION IN CANDIDATE STIRLING ENGINE HEATER HEAD TUBE ALLOYS AT 760° AND 820° C	October 1982
	6. Performing Organization Code 778-35-03
7. Author(s) John A. Misencik	8. Performing Organization Report No. E-1309
	10. Work Unit No.
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	11. Contract or Grant No.
	13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address U.S. Department of Energy Office of Vehicle and Engine R&D Washington, D.C. 20545	14. Sponsoring Agency ~~Code~~ Report No. DOE/NASA/51040-41

15. Supplementary Notes

Final report. Prepared under Interagency Agreement DE-AI01-77CS51040.

16. Abstract

Alloy tubes filled with hydrogen doped with various amounts of carbon monoxide, carbon dioxide, ethane, ethylene, methane, ammonia, or water were heated in a diesel-fuel-fired Stirling engine simulator materials test rig for 100 hours at 21 MPa and 760° or 820° C to determine the effectiveness of the dopants in reducing hydrogen permeation through the hot tube walls. Ultra-high-purity (UHP) hydrogen was used for comparison. The tube alloys were N-155, A-286, Incoloy 800, Nitronic 40, 19-9DL, 316 stainless steel, Inconel 718, and HS-188. Carbon dioxide and carbon monoxide in the concentration range 0.2 to 5 vol % were most effective in reducing hydrogen permeation through the hot tube walls for all alloys. Ethane, ethylene, methane, ammonia, and water at the concentrations investigated were not effective in reducing the permeation below that achieved with UHP hydrogen. One series of tests were conducted with UHP hydrogen in carburized tubes. Carburization of the tubes prior to exposure reduced permeation to values similar to those for carbon monoxide; however, carbon dioxide was the most effective dopant.

17. Key Words (Suggested by Author(s))		18. Distribution Statement
Hydrogen permeability	Heater tubes	Unclassified - unlimited
Superalloys	760° C	STAR Category 26
Stirling Engine	820° C	DOE Category UC-25

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified		

* For sale by the National Technical Information Service, Springfield, Virginia 22161